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ON THE RELATION BETWEEN EXTRA REFLECTIONS OF THE "SPIKE" TYPE IN LAUE PATTERNS OF NATURAL DIAMONDS AND OPTICAL PROPERTIES

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It is known that natural type I diamonds, which absorb in the infrared ($\sim 8\mu$) and ultraviolet ($\lambda < 3000$ Å) regions of the spectrum, also give anomalous extra reflections of the "spike"type on Laue patterns (^{1,2}). The nature of this effect has been discussed repeatedly in the literature ($^{3-15}$) and elsewhere. Recently it was shown that the appearance of extra reflections is connected with the presence in diamonds of special plate-like formations parallel to the faces of the cube. The existence of such formations was postulated by Frank (^{5a}), who associated them with segregations of impurity atoms. Evans and Phaal (^{13}) directly observed these formations in the study of diamonds under an electron microscope, thereby in fact demonstrating the untenability of several other hypotheses concerning the nature of the extra reflections, in particular Raman' s hypothesis (^{6}), which attributed their appearance to the interaction of X-ray and infrared quanta.

In developing his hypothesis, Frank (^{5a}) associated these formations with segregations of impurity silicon atoms. Later (^{7}) it was shown that the silicon content in diamonds is clearly insufficient to account for the observed effect. At present most authors (^{5,9,14,15}) and others tend toward the conclusion that the determining role in the appearance of extra reflections belongs to impurity nitrogen with a special layered arrangement of associated atoms, since it is precisely with high concentrations of nitrogen that the principal optical properties of type I diamonds have been linked (^{16}).

Essential information on the nature of the plate-like formations in diamonds can be obtained by a direct quantitative comparison of spike intensities with other properties for a sufficiently large number of samples. We carried out a comparison of the optical properties of more than 100 samples of natural diamonds from deposits in Yakutia with Laue patterns. The samples studied were specially selected from a much larger number according to typical optical properties (infrared absorption, ultraviolet absorption, luminescence); most of the samples were colorless transparent or semitransparent octahedra 0.9–1.5 mm thick.

The infrared absorption spectra were obtained on a UR-10 double-beam spectrometer, the ultraviolet absorption spectra on an ISP-28 spectrograph, and luminescence was observed visually upon excitation by a group of mercury lines at 365 mμ (PRK-2 lamp, UFS-3 filter). Laue patterns of the samples were taken in RKSO-type cameras using copper radiation (15 mA, 40 kV, 2 h). The orientation of the samples (direction [111] coinciding with the beam direction, [110] vertical) was carried out by an optical reflection method from a face; the average accuracy was $\pm 15'$; for samples perfect in faceting the setting accuracy was higher. A beam 0.5 mm in diameter illuminated the central part of the sample or, when necessary, any other part selected for study. The results obtained in this way were used for qualitative conclusions. To establish quantitative relations, a series of Laue patterns with the same position was initially selected.

spikes relative to the Laue spots* (the orientation is the same within 1-2′). The relative integral intensity of the spikes was determined by photometry on an MF-2 microphotometer; a correction for absorption was taken into account. To refine the quantitative relations, additional experiments were carried out using a more accurate method of orienting the sample relative to the primary beam. We used a GUR-3 goniometer (URS-50I apparatus) with a collimator giving an almost parallel beam (divergence 12′) of diameter 0.3 mm, and a device making it possible to mount a cassette with film. This made it possible to orient the crystals with respect to the primary beam with

Table 1

I.-r. spectrum (1000-1400 cm^{-1})	U.-v. spectrum	Luminescence	Spikes
1100, 1210, 1282 cm^{-1} (system *A*) + system *B* (Fig. 1a)	Absorption $\lambda < 3000$ Å with structure at the edge of the band (correlates with the i.-r. spectrum)	Blue, bright, medium, weak. Pink weak. Absent	Present, proportional in intensity to the i.-r. band 1368 cm^{-1} (system *B*)
Does not absorb	Transparent to 2250 Å	Blue medium, weak. Yellow medium, weak. Absent	No
1010, 1100, 1175, 1331 cm^{-1} (system *B*) (Fig. 1b)	System of bands 2410-2250 Å (correlates with the i.-r. spectrum)	Yellow-green. Whitish	No

I.-r. spectrum (1000-1400 cm^{-1})	U.-v. spectrum	Luminescence	Spikes
1010, 1100, 1175, 1331, 1368 cm^{-1} (system B) (Fig. 1b)	System of bands 2410-2250 Å. Bands of stepwise type in the region 2900-2500 Å	Yellow-green. Blue	Present, proportional in intensity to the i.-r. band 1368 cm^{-1}

an accuracy no worse than 2′. The intensities of the spikes of all diamonds were reduced to a single value by selecting the exposure, the reciprocal of which (with correction for absorption) was used subsequently as a quantitative measure of the spike intensity. It should be noted that the two methods gave very close results.

Comparison of the optical properties of diamonds with their Lauegrams had also been carried out previously ([3,8,12,15]). However, in those studies most often only one property was examined, for example luminescence ([8,12]) or u.-v. absorption ([3,15]), and the number of objects studied in a number of cases was small. In work ([8]) a certain connection was noted between the intensities of the spikes and the luminescence of diamonds. The results for u.-v. absorption of diamonds proved contradictory. Thus, whereas in work ([3]) the absence of correlation between spikes and u.-v. absorption was shown, Takati and Lang ([15]) found such a correlation over zones of one and the same crystal on several samples. They relate the failures of previous comparisons to the failure to take into account the zonal structure of diamonds, as a result of which different zones of a crystal, possessing different properties, could be studied by optical and X-ray methods. We note that the method used in the present work is, to a significant extent, free of this drawback, since both in the study of optical absorption and in the recording of Lauegrams one and the same central part of the crystal was studied; the zonality of the samples was monitored by absorption and luminescence.

The results we obtained are summarized in Table 1. To illustrate the quantitative relations, Fig. 2 compares the relative intensities of the spikes with the absorption coefficients of the principal bands in the i.-r. spectra of diamonds: 1282 cm^{-1}, directly connected with the conten-

* The spikes associated with the point (111) of reciprocal space were studied.

by impurity nitrogen ([16]), 1175 cm^{-1}, characteristic of intermediate diamonds ([20]), and 1368 cm^{-1}. Since the absorption of diamonds in the ultraviolet region of the spectrum correlates with infrared absorption (see Table 1), from the graphs presented one can also establish the degree of correlation of the spikes with ultraviolet absorption.

It follows convincingly from Fig. 2a that there is no correlation of the spikes with the infrared band at 1282 cm^{-1}, i.e., with the total content of impurity nitrogen. Thus, the currently widespread opinion that impurity nitrogen is for the most

Fig. 1 and Fig. 2

Figure 1: Fig. 1 and Fig. 2

part located in the diamond structure precisely in platelet formations should be considered erroneous. At the same time, the nonparamagnetic character of most nitrogen atoms in colorless diamonds (17,18) clearly contradicts its predominant occurrence in the form of single centers. Apparently, the solution of the question should be sought in the assumption of the existence of disordered associations of the N_2 type or others.

Fig. 1. Infrared spectra of diamonds: a—system of absorption bands A; the bands of system B are marked by arrows; b and v—infrared spectra of diamonds of the intermediate type (system B).

Fig. 2. Dependence of the intensity of the spikes on the absorption coefficients of the infrared spectra of diamonds. The points at the origin correspond to several dozen specimens. The coefficients for the bands 1282 and 1175 cm^{-1} were determined taking into account the superposition of two systems (Fig. 1). a—$\nu = 1282$ cm^{-1}; b—1175 cm^{-1}; v—1368 cm^{-1}.

There is also no connection between the intensity of the spikes and the 1175 cm^{-1} band, the principal one in the series characteristic of intermediate-type diamonds (Fig. 2b). On the other hand, a connection is quite clearly revealed between the spikes and the intensity of the 1368 cm^{-1} band, which, as a rule, accompanies the system of "nitrogen" bands in type I diamonds* and sometimes appears together with the system of bands of "intermediate" diamonds. The nitrogen and intermediate diamonds fit quite satisfactorily on one straight line. Rotation of the crystals near the initial position (about the [110] axis) showed that the regions of reciprocal space giving extra reflections are exactly the same both for nitrogen-bearing and for intermediate diamonds.

The correlation found can also be illustrated by the example of zonal diamonds with a colorless core and a lemon-yellow shell. Thus, the yellow shell, as a rule, gives no spikes on Lauegrams (11); at the same time, in the IR spectrum the 1368 cm^{-1} band is absent, although the nitrogen band at 1282 cm^{-1} is very intense (19). On the contrary, in the IR spectra of diamonds with a high content of plate-like formations, investigated by Evans and Phaal (13), the absorption coefficient of the 1368 cm^{-1} band is high. Let us also note the considerable variations in the frequency of the maximum of this band from sample to sample (1358–1378 cm^{-1})*; this can be compared with the differences in the plate-like formations observed by Evans and Phaal (13).

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* It is precisely with this that the constant observation of spikes in type I diamonds is connected.

The result obtained makes it possible to critically reconsider correlations established by other authors. Our data show that a correlation of the intensities of extra reflections with any properties may occur insofar as the 1368 cm^{-1} band correlates with these properties. Thus, for example, we earlier noted ([20]) a certain statistical connection between the 1368 cm^{-1} band and the luminescence of diamonds. This, apparently, is also related to the observation of the authors of ([8])**. Further, the 1368 cm^{-1} band in the IR spectra of diamonds never appears independently, but only accompanies other systems of bands; in particular, as a rule, it accompanies the system of impurity-nitrogen bands (1282 cm^{-1}), and with increasing intensity of this system the intensity of the 1368 cm^{-1} band also often increases. This circumstance may in principle explain the correlation between spikes and UV absorption (although far from a strict one) noted by Takagi and Lang ([15]).

Thus, the experimental data obtained by us show the need to reconsider the established ideas concerning the predominant state of nitrogen in natural diamonds. At the same time, however, the participation of some part of the nitrogen in the plate-like formations is not excluded. Clarification of this question requires further investigations.

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* For the samples in Fig. 2 the position of the maximum varies within the limits 1366–1371 cm^{-1}; however, for most of them it is constantly 1368 cm^{-1}.

** Investigation of a large number of samples (see Table 1) shows that there is no direct connection between spikes and luminescence.

Note: Figure translations are in progress. See original paper for figures.